Solution state and complexing ability of 1,4-bis(amidomethylsulfinyl)butane toward iron(III), copper(II), cobalt(II), nickel(II), and manganese(II)

V. V. Neklyudov,[a] G. A. Boos,[a] M. M. Shulaeva,[b] G. A. Chmutova,[a] Yu.I. Bagina,[a] Yu. I. Salnikov,[a] and R. R. Amirov[a]*

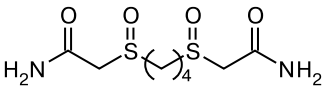
[a]*Kazan (Volga region) Federal University, 18 ul. Kremlevskaya, 420008 Kazan, Russian Federation. E-mail: sacredbox@hotmail.com*

[b]*A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center of the Russian Academy of Sciences, 8 ul. Akad. Arbuzova, 420088 Kazan, Russian Federation*

The solution state and thermodynamic stability of complexes of the new antituberculosis agent 1,4-bis(amidomethylsulfinyl)butane (**L**) with iron(III), copper(II), cobalt(II), nickel(II), and manganese(II) in an aqueous solution in the presence and in the absence of the nonionic surfactant Brij 35 were studied by spectrophotometry, pH potentiometry, NMR relaxation technique (T = 25 °C; variable ionic strength), and mathematical simulation. The geometry optimization of all structures was carried out by the molecular mechanics method MM2 in order to obtain data on coordination modes. In addition, the structure of 1,4-bis(amidomethylsulfinyl)butane was refined by the DFT/B3LYP/6-311++G(d,p) quantum chemical method using the IEFPCM model to take into account solvent effects. In an aqueous solution (in the concentration range of $1.3 \cdot 10^{-5}$—$1 \cdot 10^{-3}$ mol L^{-1}) and in the presence of Brij 35, 1,4-bis(amidomethylsulfinyl)butane exists as a neutral monomer. The Beer—Lambert—Bouguer law is obeyed in a wide concentration range for compound **L** in an aqueous solution, as well as in the presence of the surfactant, which can be used for the quantification of compound **L**. Iron(III), cobalt(II), and nickel(II) were shown to form 1 : 1 mononuclear complexes with **L**; and copper(II) forms, 1 : 1 and 2 : 2 complexes. The presence of Brij 35 in the Cu^{2+}—**L** system at a micellar concentration promotes the formation of a dinuclear complex.

Key words: 1,4-bis(amidomethylsulfinyl)butane, iron(III), copper(II), cobalt(II), nickel(II), manganese(II), nonionic surfactant Brij 35, complexation, three-dimensional structure.

In the present work, we studied iron(III), copper(II), cobalt(II), nickel(II), and manganese(II) complexes with 1,4-bis(amidomethylsulfinyl)butane (**L**).



L

As part of continuing research on the synthesis of antituberculosis agents performed at the A. E. Arbuzov Institute of Organic and Physical Chemistry of the Kazan Scientific Center of the Russian Academy of Sciences, we synthesized and patented the new compound — 1,4-bis(amidomethylsulfinyl)butane.[1] Previously, we studied the protolytic and complexing properties of compounds of the triazine series, such as 2,4-diamino-6-(carbamoylmethylsulfinylmethyl)-1,3,5-triazine and 2,4-diamino-6-(acetohydrazidomethylsulfinylmethyl)-1,3,5-triazine,[2,3] as well as of 1-[5-(hydrazidomethylsulfinyl)pentyl]-3,5-dimethyl isocyanurate,[4,5] in an aqueous dimethyl sulfoxide solution These data are absent for 1,4-bis(amidosulfinyl)alkanes, in particular, for bis(amidomethylsulfinyl)butane. Meanwhile, knowledge of these properties is useful for the prediction of the behavior of these compounds and their application in biology, pharmacology, and medicine.

The goal of this work is to study the solution state and the protolytic and complexing properties of the new antituberculosis agent 1,4-bis(amidomethylsulfinyl)butane toward biometals of different nature (iron(III), copper(II), cobalt(II), nickel(II), and manganese(II)). Besides, the aim was to assess the structures of different forms of this compound and evaluate its donor properties (coordination modes) in complexes by the molecular mechanics method MM2.

Experimental

Compound **L** was synthesized and identified by a known procedure.[1] A white crystalline compound, m.p. 148—149 °C, was obtained. Found (%): C, 35.64; H, 5.79; N, 10.12; S, 23.77.

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